Application of the zero separation theorem to the restricted primitive model of electrolyte solutions

Sloth, Peter

Published in:
Journal of Chemical Physics

Link to article, DOI:
10.1063/1.455651

Publication date:
1988

Document Version
Publisher's PDF, also known as Version of record

Application of the zero separation theorem to the restricted primitive model of electrolyte solutions

Peter Sloth
Fysisk-Kemisk Institut and Center for Modellering, ikke-lineære systemers Dynamik og Irreversibel Termodynamik (MIDIT), Technical University of Denmark, Bldg. 206, DK 2800 Lyngby, Denmark

(Received 17 May 1988; accepted 11 July 1988)

Calculations of activity coefficients by application of the zero separation theorem is discussed for the restricted primitive model of electrolyte solutions. Numerical results within the framework of the hypernetted chain approximation are given. These indicate that the bridge functions—at zero separation—as a first approximation might be quite well represented by the corresponding function for an uncharged hard sphere system.

I. INTRODUCTION

In this paper the so-called zero separation theorem (ZST) is applied to the restricted primitive model (RPM) of electrolyte solutions.

In the RPM the total potential energy is given by a sum of pair potentials only. Let $g_{ij}(\mathbf{r}_{12})$ and $u_{ij}(\mathbf{r}_{12})$ be the radial distribution function and the pair potential function, respectively, between a particle of species i at $\mathbf{r}_1$ and a particle of species j at $\mathbf{r}_2$. The ZST then gives a relationship between a thermodynamic property of the system and the limit $r \to 0$ of $y_{ij}(\mathbf{r}_{12}) \equiv g_{ij}(\mathbf{r}_{12}) \exp[u_{ij}(\mathbf{r}_{12})/kT]$. ($T$ is the absolute temperature and k Boltzman's constant.) The ZST was first worked out explicitly for the one-component hard sphere system[1,2] in the 1960's and has more recently been discussed for systems with long-range forces.[3]

In Sec. II the calculation of activity coefficients for the RPM—by application of the ZST—is discussed in some details within the framework of the hypernetted chain (HNC) approximation.[4–6] In Sec. III numerical results—based on the HNC theory—are given, and it is found that although the HNC approximation may yield good results for $y_{ij}(\mathbf{r}_{12})$, for large values of r, this is not necessarily the case for $r \approx 0$. It should be noted that a similar conclusion has been reached in the case of neutral hard sphere systems some years ago.[7] We find, however, that a simple approximation concerning the "bridge functions"—at $r \approx 0$—gives a marked improvement of the results.

II. THEORY

As a convenient starting point, we shall use a result derived by Tenne *et al.*[3] Consider an overall electroneutral system—with volume V—of N hard, charged spheres ($N/2$ cations and $N/2$ anions) in a "solvent" of N_h neutral hard spheres (with the same dielectric permittivity ϵ as the surrounding media). All the species are taken to have the same diameter, a. Let $+$, $-$, and h denote cations, anions, and neutral hard spheres, respectively. The pair potential functions $u_{ij}(\mathbf{r}_{12}) = u_{ij}(r)$ in this system are then given by

$$u_{++}(r) = u_{--}(r) = u^{\mathrm{HS}}(r) + (ze)^2/4\pi\epsilon r, \tag{1a}$$

$$u_{+-}(r) = u^{\mathrm{HS}}(r) - (ze)^2/4\pi\epsilon r, \tag{1b}$$

$$u_{h+}(r) = u_{h-}(r) = u_{hh}(r) = u^{\mathrm{HS}}(r). \tag{1c}$$

In Eqs. (1) e is the electron charge and z the valence number of the electrolyte. $u^{\mathrm{HS}}(r)$ is the hard sphere pair-potential function, defined by

$$u^{\mathrm{HS}}(r) = \begin{cases} \infty, & r < a \\ 0, & a \leqslant r \end{cases}. \tag{2}$$

We notice that systems defined through Eqs. (1) become identical to the RPM of electrolyte solutions in the limit $\rho_h \equiv N_h/V \to 0$. According to Tenne *et al.*,[3] the ZST for the mixture of hard charged spheres and hard neutral spheres, specified by Eqs. (1), might be given as

$$\ln y_{\pm} = \ln[y_{+-}(0) y_{\alpha h}(0)]^{1/2}. \tag{3}$$

In Eq. (3) $y_{\pm}$ is the molar mean ionic activity coefficient of the electrolyte [not to be confused with the function $y_{+-}(r)$], and the index α may be either $+$, $-$, or h. $y_{ij}(r)$ can be expressed by the following exact relation[4]:

$$\begin{aligned} y_{ij}(r) &= \exp[\gamma_{ij}(r) + B_{ij}(r)], \\ \gamma_{ij}(r) &\equiv h_{ij}(r) - c_{ij}(r), \end{aligned} \tag{4}$$

where $c_{ij}(r)$ are the direct correlation functions, $B_{ij}(r)$ the bridge functions, and $h_{ij}(r) = g_{ij}(r) - 1$. $c_{ij}(r)$ and $h_{ij}(r)$ are related via the Ornstein–Zernike (OZ) equation:

$$\gamma_{ij}(\mathbf{r}_{12}) = \sum_k \rho_k \int c_{ik}(\mathbf{r}_{13}) h_{kj}(\mathbf{r}_{23}) d\mathbf{r}_3. \tag{5}$$

In Eq. (5) the summation is taken over all species in the system.

The HNC approximation is obtained by setting $B_{ij}(r) = 0$.[4,5] This seems to be a reasonable approximation for $r \geqslant a$ but less so for $r < a$, as will be shown later on. Equation (4) might be rewritten as

$$\begin{aligned} y_{ij}(r) &= y_{ij}^{\mathrm{HS}}(r) \exp[\Delta\gamma_{ij}(r) + \Delta B_{ij}(r)], \\ \Delta\gamma_{ij}(r) &\equiv \gamma_{ij}(r) - \gamma_{ij}^{\mathrm{HS}}(r), \\ \Delta B_{ij}(r) &\equiv B_{ij}(r) - B_{ij}^{\mathrm{HS}}(r), \end{aligned} \tag{6}$$

where the HS indicates functions for the corresponding uncharged hard sphere system.

Setting $\Delta B_{ij}(r) = 0$ in Eq. (6) corresponds to the reference HNC (RHNC) approximation[8]—with the uncharged hard sphere system as the reference system—and this seems to be a less drastic approximation than setting $B_{ij}(r) = 0$.

 0021-9606/88/205078-03$02.10

From Eqs. (3) and (6) we find, using the exact relation[1,2] $y^{HS}(0) = y_{\pm}^{HS}$,

$$\ln y_{\pm} = \ln y_{\pm}^{HS} + (1/2)[\Delta\gamma_{+-}(0) + \Delta\gamma_{ah}(0)] + (1/2)[\Delta B_{+-}(0) + \Delta B_{ah}(0)]. \quad (7)$$

If the last term in Eq. (7) is neglected, we finally obtain

$$\ln y_{\pm} \simeq \ln y_{\pm}^{HS} + (1/2)[\gamma_{+-}(0) + \gamma_{ah}(0)] - \gamma^{HS}(0). \quad (8)$$

From Eq. (5) we find in the limit $\rho_h \to 0$ ($\rho \equiv N/V$):

$$\gamma_{+h}(\mathbf{r}_{12}) = (\rho/2)\int \{c_{++}(\mathbf{r}_{13})h_{+h}(\mathbf{r}_{32}) + c_{+-}(\mathbf{r}_{13})h_{-h}(\mathbf{r}_{32})\}d\mathbf{r}_3$$

or

$$\gamma_{+h}(\mathbf{r}_{12}) = \rho\int c_A(\mathbf{r}_{13})h_{+h}(\mathbf{r}_{32})d\mathbf{r}_3, \quad (9)$$

where

$$c_A(r) \equiv (1/2)[c_{++}(r) + c_{+-}(r)].$$

Equation (9) might be used in connection with a suitable approximative relation between $\gamma_{+h}(\mathbf{r})$ and $h_{+h}(\mathbf{r})$ to obtain $\gamma_{+h}(0) = \gamma_{ah}(0)$. {In the case of the HNC approximation we, i.e., have the following closure: $h_{+h}(r) = \exp[\gamma_{+h}(r)] - 1$ for $a \leqslant r$ and $h_{+h}(r) = -1$ for $r < a$.}

In order to apply Eq. (8) in actual calculations, we need to know the *exact* hard sphere quantities $\ln y_{\pm}^{HS}$ and $\gamma^{HS}(0)$. The Carnahan–Starling equation of state[9] provides an accurate expression for $\ln y_{\pm}^{HS}$:

$$\ln y_{\pm}^{HS} = \eta(8 - 9\eta + 3\eta^2)/(1-\eta)^3, \quad (10)$$

where

$$\eta \equiv \pi\rho a^3/6.$$

For the calculation of $\gamma^{HS}(0)$ one might—as a first approximation—use the analytical expression obtained by the Percus–Yevick (PY) theory[10,11]:

$$\gamma^{HS}(0) = -[1 + c^{HS}(0)] \simeq (1+2\eta)^2/(1-\eta)^4 - 1. \quad (11)$$

The PY theory is found to yield a good approximation to $c(r)$ for neutral hard spheres—at densities that are not too high—and we believe that formula (11) is quite accurate in the density regime which is investigated in this work. This is supported by comparison of values obtained by Eq. (11) with the data based on Monte Carlo (MC) calculations given by Groot *et al.*[12] For $\rho a^3 = 0.2$, which correspond to the highest density studied in this work, Eq. (11) is found to reproduce the MC result with the three significant digits given in Ref. 12.

TABLE I. $\gamma_{+-}(0)$ and $\gamma_{ah}(0)$ values obtained by the HNC approximation for $B = 1.681$.

ρ^*	$\gamma_{+-}(0)$	$\gamma_{ah}(0)$
0.000 842 4	−0.1970	0.0035
0.009 595	−0.4980	0.0406
0.039 30	−0.6835	0.1750
0.092 48	−0.6460	0.4573
0.181 9	−0.2523	1.087

In passing, we also note that if $\gamma_{+-}(0)$ and $\gamma_{ah}(0)$ results given by the mean spherical approximation[13] are inserted into Eq. (8), we find

$$\ln y_{\pm} \simeq \ln y_{\pm}^{HS} - \frac{(ze)^2}{4\pi\epsilon kTa}\frac{x + 1 - (1+2x)^{1/2}}{x} + (1+2\eta)^2/(1-\eta)^4 - 1 - \gamma^{HS}(0),$$

where $x \equiv \kappa a$, κ being the inverse Debye–Hückel length. By application of Eq. (11) the above equation reduces to the traditional MSA result as found from the energy equation.

III. NUMERICAL RESULTS

We have calculated $\gamma_{+-}(0)$ — and $\gamma_{+h}(0) = \gamma_{ah}(0)$ values by the HNC approximation for parameters corresponding to aqueous 1:1 electrolytes. It should be pointed out that application of the HNC theory—in connection with Eq. (8)—is not inconsistent with the assumption $B_{ij}(0) = B_{ij}^{HS}(0)$, since $B_{ij}(r)$ is undefined for $r < a$ in the numerical solution of the HNC approximation.

In the RPM, an electrolyte is completely specified by two dimensionless parameters, $\rho^* \equiv \rho a^3$ and $B \equiv (ze)^2/4\pi\epsilon kTa$. In Table I results for $\gamma_{+-}(0)$ and $\gamma_{ah}(0)$ are given for $B = 1.681$ and five different concentrations in the range $0.000\,842\,4 < \rho^* < 0.181\,9$.

In Table II are given $\ln y_{\pm}$ results obtained by these values and Eqs. (8)–(11), as well as results from the "true" HNC expression [$B_{ij}(0) = 0$]:

$$\ln y_{\pm}^{HNC} = (1/2)[\gamma_{+-}(0) + \gamma_{ah}(0)]. \quad (12)$$

For comparison some MC data from two independent sources are also given. The data indicated MC_{MS} are obtained from values of the Helmholtz free estimated by multistage sampling MC[14] and the osmotic coefficients given in Ref. 15. Data indicated MC_{test} was obtained by direct MC

TABLE II. $\ln y_{\pm}$ values obtained by different approaches for $B = 1.681$.

ρ^*	HNC	Eqs. (8)–(11)	MC_{MS}	MC_{test}
0.000 842 4	−0.0968	−0.0968		
0.009 595	−0.229	−0.229	−0.227 ± 0.003	−0.228 ± 0.002
0.003 930	−0.254	−0.261	−0.264 ± 0.005	
0.092 48	−0.094	−0.136	−0.128 ± 0.006	
0.181 9	0.417	0.224	0.255 ± 0.010	0.253 ± 0.006

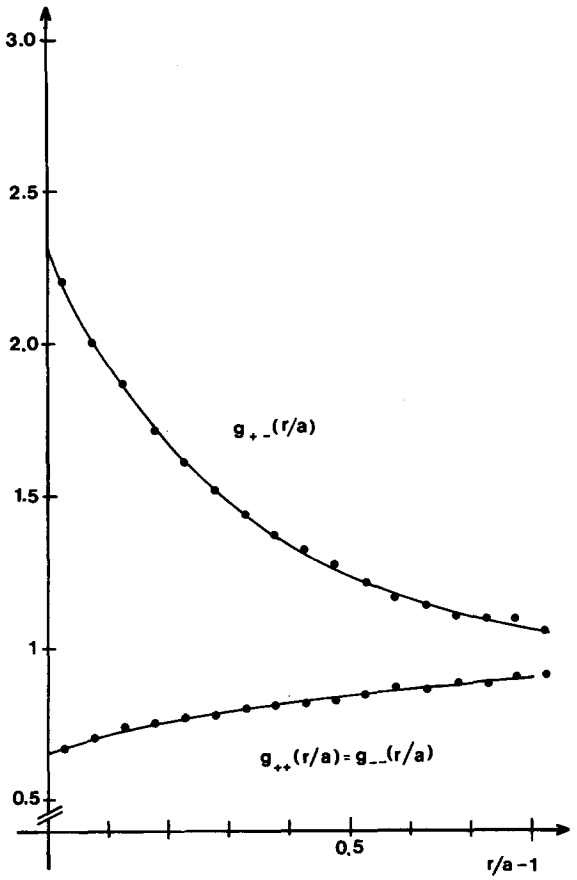

FIG. 1. Comparison of radial distribution functions obtained by the HNC approximation (full line) and a MC simulation with 256 cations and 256 anions[17] (closed circles). $B = 1.681, \rho^* = 0.1819$.

simulations of the excess chemical potentials by application of the "test-particle" formula of Widom.[16]

From Table II it is seen, that Eqs. (8)–(11)—with application of HNC results for $\gamma_{ij}(0)$—do indeed give better results for $\ln y_{\pm}$ than the HNC approximation itself, at the higher concentrations. At the highest concentration the HNC result is about 65% in error, whereas the assumption $B_{ij}(0) = B^{HS}(0)$ gives a result which is "only" about 10% in error. This indicates that the bridge functions—at $r \approx 0$—might be quite well approximated by $B_{ij}(r) \simeq B^{HS}(r)$. We also note that even though the HNC approximation fails to some extent at $r \approx 0$, it is a good approximation for $r \geqslant a$ (outside the hard core). This is readily seen from Fig. 1 where HNC results for the radial distribution functions, for the most dense system studied here, are compared with MC results. The agreement between the HNC and MC functions is indeed excellent!

IV. CONCLUSION

The results obtained in this paper indicate that the bridge functions—for the RPM—might be rather well represented by the corresponding functions for a uncharged hard sphere system, at least for small values of r. This further suggests that the RHNC—with the neutral hard sphere system as the reference system—may yield a more consistent approximation than the HNC.

Finally we note that even though the ZST might not provide the most accurate route to $\ln y_{\pm}$—for a given approximation—it may be used as a quite sensitive test on the validity of different kinds of approximations.

ACKNOWLEDGMENTS

I acknowledge useful discussions with Dr. T. S. Sørensen as well as financial support from Teknologistyrelsen (The National Agency for Technology) and Thomas B. Thriges Fund.

[1]W. G. Hoover and J. C. Poirier, J. Chem. Phys. **37**, 1041 (1962).
[2]E. Meeron and A.J. F. Siegert, J. Chem. Phys. **48**, 3139 (1968).
[3]R. Tenne, B. Barboy, S. Baer, and M. Silbert, Mol. Phys. **47**, 913 (1982).
[4]J. M. J. van Leeuwen, J. Groeneveld, and J. DeBoer, Physica **25**, 792 (1959).
[5]E. Meeron, J. Math. Phys. **1**, 192 (1960).
[6]J. C. Rasaiah and H. L. Friedman, J. Chem. Phys. **48**, 2742 (1968).
[7]D. Henderson and E.W. Grundke, J. Chem. Phys. **63**, 601 (1975).
[8]F. Lado, Phys. Rev. A **135**, 1013 (1964).
[9]N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969).
[10]J. K. Percus and G. J. Yevick, Phys. Rev. **100**, 1 (1958).
[11]M. S. Wertheim, Phys. Rev. Lett. **10**, 321 (1963).
[12]R. D. Groot, J. P. van der Eerden, and N. M. Faber, J. Chem. Phys. **87**, 2263 (1987).
[13]E. Waisman and J. L. Lebowitz, J. Chem. Phys. **56**, 3093 (1972).
[14]J. P. Valleau and D. N. Card, J. Chem. Phys. **57**, 5457 (1972).
[15]J. C. Rasaiah, D. N. Card, J. P. Valleau, J. Chem. Phys. **56**, 248 (1972).
[16]P. Sloth and T. S. Sørensen, Chem. Phys. Lett. **143**, 140 (1988).
[17]P. Sloth (unpublished work).